THE AMERICAN
JOURNAL OF PHARMACY

MAY, 1910

A NOTE ON A SUITABLE ULTIMATE STANDARD FOR THE VOLUMETRIC SOLUTIONS OF THE U. S. PHARMACOPŒIA.

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The very prominent position given to volumetric analysis in the U. S. Pharmacopœia, and its almost exclusive use, wherever possible, in determining whether a given substance comes up to the required standard of purity, render it imperative that the most suitable ultimate standard be adopted for the necessary volumetric solutions. It is also obvious that in considering what substance might form a suitable ultimate standard for these solutions, we must place as of primary importance the readiness with which such substance is obtainable in a pure state, its stability under ordinary conditions, its possessing the necessary properties for admitting of its use in a volumetric process of proven accuracy, and, finally, what likelihood there is of different operators obtaining such substance in different degrees of purity although working by the same method.

The substance chiefly relied on as standard in the present U.S.P., namely, potassium bitartrate, although meeting these requirements quite satisfactorily in many ways, nevertheless appears to present the disadvantage of introducing a personal error in the procedure for its purification. Thus Parsons,[1] who investigated the suitability of this substance as a means for the standardization of acid and alkaline solutions, states that he "made up some according to the directions given . . . but found it necessary, in order to get the pure salt, to crystallize three times in addition." He also

[1] *Jour. Anal. Chem.*, **6**, 380–381 (1892).

states that this salt has a "tendency to retain an excess of acid, probably tartaric, set free in small quantity by the hot hydrochloric acid."

The more or less undecided state of this question of the most suitable substance for use in standardizing volumetric solutions may also be seen from the very large number of substances which have been proposed for such use by different authors.[2] Thus for standardizing acids and alkalies, Reinitzer (*Zeit. anal. Chem.*, **34**, 575) uses sodium carbonate; Grandeau (*Ibid.*, **2**, 426) and also Pincus (*Ibid.*, **2**, 426) use Iceland spar; Sörensen (*Ibid.*, **40**, 115) uses sodium oxalate; Rimbach (*Ibid.*, **32**, 449) uses borax; Hartley (*Ibid.*, **12**, 89) uses metallic sodium; Seyda (*Ibid.*, **39**, 458) and also Weinig (*Ibid.*, **32**, 450) use ammonium chloride; Knublauch (*Ibid.*, **21**, 165) uses ammonium sulphate; Fessel (*Ibid.*, **38**, 449) uses potassium iodate; Reichardt (*Ibid.*, **13**, 49) uses oxalic acid; Ulbricht and Meissl (*Ibid.*, **26**, 350) use potassium tetroxalate; Bornträger (*Ibid.*, **25**, 333) uses potassium bitartrate; Richter (*Ibid.*, **21**, 205) uses potassium dichromate; Meineke (*Ibid.*, **35**, 338) uses potassium biniodate; Guyard (*Ibid.*, **24**, 585) uses boric acid; Petersen (*Ibid.*, **41**, 165) uses succinic acid; Riegler (*Ibid.*, **35**, 308; **38**, 250) uses iodic acid; while Hart and Croasdale (*Ibid.*, **31**, 190; **33**, 455) obtain a standard sulphuric acid solution by electrolyzing pure copper sulphate.

Similarly, for standardizing potassium permanganate, Riegler (*Ibid.*, **35**, 522) uses oxalic acid; Ulbricht and Meissl (*Ibid.*, **26**, 350) use potassium tetroxalate; Sörensen (*Ibid.*, **41**, 169) uses sodium oxalate; Gräger (*Ibid.*, **6**, 209) uses ferrous oxalate; Stolba (*Ibid.*, **18**, 600) uses lead oxalate; Schöne (*Ibid.*, **18**, 137) uses piano (iron) wire; Pawolleck (*Ibid.*, **41**, 172) uses ferrous ammonium sulphate; Biltz (*Ibid.*, **41**, 173) uses ferrous sodium sulphate; Gintl (*Ibid.*, **6**, 447) uses potassium ferrocyanide; Wdowiszewski (*Ibid.*, **41**, 174) uses iron oxide; while Erlenmeyer (*Ibid.*, **18**, 291) uses lead sulphocyanate. For standardizing iodine solutions, Kalmann (*Ibid.*, **26**, 728) uses sodium sulphite; Bobierre (*Ibid.*, **8**, 505) uses sodium arsenate; Zulkowsky (*Ibid.*, **41**, 184) uses potassium dichromate; Crismer (*Ibid.*, **25**, 553) uses normal potassium chro-

[2] A very useful contribution to the literature on this subject, which has been freely made use of in this connection, is a paper by Vanino and Seitter in *Zeit. anal. Chem.*, **41**, 141–218 (1902).

mate; Riegler (*Ibid.*, **35**, 305) uses iodic acid; Fessel (*Ibid.*, **41**, 187) uses potassium iodate; Meineke (*Ibid.*, **35**, 338) uses potassium biniodate; Kratschmer (*Ibid.*, **24**, 546) uses sodium bromate; while Metzl (*Jour. Chem. Soc.*, **90**, ii, 194) uses potassium antimonyl tartrate.

We may, perhaps, also gain an idea as to some of the reasons why apparently not a single one of the substances above mentioned has met with entire satisfaction generally, if we recall some of the remarks made by various authors concerning some of the substances in the above list which appear to have been used most. Thus, according to Morse,[3] the substance which has been longest and probably most frequently employed for the standardization of acids is the neutral anhydrous carbonate of sodium. The latter is also recommended by Sutton.[4] As is well known, however, this salt is hygroscopic and hence great care must be taken in handling it. Thus, according to Morse, the portion of the material which is to be used in any experiment should be reheated in a small platinum crucible or boat, cooled in a desiccator, and protected from the moisture of the air while weighing by inclosing it in a weighing glass. It has also the disadvantage that it is liable to appreciable decomposition if the temperature is not strictly regulated while it is being heated in order to convert all the bicarbonate into the normal salt. Thus, according to Seyda,[5] sodium carbonate is likely to retain excess of CO_2, or if overheated it may contain sodium hydroxide. Similarly, in the case of potassium tetroxalate, which is recommended for standardizing purposes by Kühling[6] and also by Morse,[7] Lunge[8] states that he has never been able to prepare a potassium tetroxalate in which the water of crystallization corresponds accurately with the formula $C_2O_4HK.C_2O_4H_2.2H_2O$. In the case of oxalic acid, the disadvantages which may be mentioned, on the authority of Morse,[9] are that the commercial article contains acid oxalates from which it cannot be readily freed by the ordinary process of recrystallization from water and that it cannot be dried

[3] Morse: Exercises in Quantitative Chemistry (1905), p. 127.
[4] Sutton: Volumetric Analysis, 9th ed., p. 42.
[5] *Jour. Chem. Soc.*, **78**, ii, 44 (1900).
[6] Ibid., **86**, ii, 80 (1904)
[7] Morse: Exercises in Quantitative Chemistry (1905), p. 126.
[8] *Jour. Chem. Soc.*, **86**, ii, 771 (1904).
[9] Morse: Exercises in Quantitative Chemistry (1905), pp. 116–117.

in a desiccator, since in an atmosphere devoid of moisture it loses water of crystallization. Finally, Iceland spar, which has recently been advocated by Rose,[10] has the disadvantage that much of the material now sold under that name contains magnesium carbonate.[11]

On the other hand, of all the volumetric processes at present known, there is probably not one that excels in elegance [12] or accuracy the well-known Volhard method for titrating silver by means of a thiocyanate solution. In fact, its advantages are so pronounced that Shutt and Charlton [13] have even recommended its use in estimating the very small amounts of chlorine in potable waters, in preference to the standard chromate method; while the maximum error of Rosanoff and Hill,[14] when applying this method to the estimation of chlorides by precipitating with a known excess of silver and determining the remaining silver in the filtrate, was only 0.17 per cent. Finally, we need only mention the fact that Stas,[15] in his classical atomic weight work, did not estimate silver or chlorine gravimetrically but by titration by the method of Gay-Lussac. Likewise, Richards,[16] in his revision of Stas' work, estimated silver and chlorine by titration with the aid of his nephelometer. It is thus seen that the experience of chemists has been that, in the case of silver, the available volumetric methods may even exceed in accuracy the gravimetric process; while the high value of the latter, as a means for standardizing volumetric solutions, has been expressed by more than one author.[17] If, therefore, we should base the standardization of all, or at least most, of our

[10] *Chem. Eng.*, **10**, 204–206 (1909).

[11] Morse: Exercises in Quantitative Chemistry (1905), p. 125.

[12] Vanino and Seitter express themselves in such connection as follows: "Hierher zählen bekanntlich die elegantesten und genauesten Methoden der Maassanalyse, wie wir solche in denjenigen von Gay-Lussac, Mohr, Volhard, und Liebig besitzen und welchen sammtlich eine—Silbernitratlosung —zu Grunde liegt."—*Zeit. anal. Chem.*, **41**, 194, (1902).

[13] *Jour. Chem. Soc.*, **90**, ii, 894 (1906).

[14] *Jour. Amer. Chem. Soc.*, **29**, 273 (1907).

[15] Richards: *Ibid.*, **27**, 461 (1905).

[16] *Jour. Amer. Chem. Soc.*, **27**, 502–510 (1905).

[17] Parsons: "I have no hesitancy, when convenience is also taken into consideration, in placing the determination as silver chloride at the head of gravimetric methods," for standardization purposes.—*Jour. Anal. Chem.*, **6**, 373–374 (1892). Phelps and Hubbard: "The previously most valued standard—hydrochloric acid standardized gravimetrically as silver chloride." —*Amer. Jour. Sci.*, **23**, iv, 213 (1907).

volumetric solutions on this method, we would obtain not only convenience and general ease of manipulation but also a very high degree of accuracy.

As to the comparatively great ease of obtaining pure metallic silver we need only mention the following facts. In his revision of Stas' atomic weight for chlorine, one of the samples of silver which Richards [18] used was sent to him from the Colorado Smelting Works at Argo, Colorado. This specimen was stated to be the product of the treatment of ores in which it occurs associated with quartz, barite, calcite, pyrite, sphalerite, with more or less copper in the form of chalcopyrite, together with small amounts of arsenic, antimony, lead, bismuth, and tellurium. To recover the silver, the ore is roasted, mixed with other ores which are chiefly siliceous, and the mixture is so arranged that when smelted it yields a slag, containing about 40 per cent. of silica, and a first matte of fusible sulphide, which assays about 40 per cent. of copper, 10 per cent. of lead, and 400 ounces of silver and 6 ounces of gold per ton. The next stage in the process includes the roasting and concentration of the ore-metal, or first matte, to "white metal" containing about 60 per cent. of copper. The silver is then extracted from this white metal by the following operations: Rough roasting, fine grinding, fine roasting for sulphate of silver by Ziervogel's process, leaching and the precipitation of the silver on plates of copper. In the precipitation of the silver a certain amount of copper is found mixed with the silver in the form of cuprous oxide and of small scales and scraps of metallic copper. This copper is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by means of a small jet of steam. Sulphate of copper is thus formed, which is carefully washed out of the silver. The silver is then dried and melted into bars of an average fineness of 99.9 per cent. The specimen of silver actually obtained by Richards, however, the latter found to be even purer than is indicated by the above figures. We thus see that although starting with a very complex natural mixture, containing many different elements, only a very small fraction of which is the desired silver, this metal is actually obtained on a large commercial scale of a degree of purity almost approaching absolute purity. Can this be said of any of the other numerous substances which have been proposed as standards in volumetric analysis?

[18] *Jour. Amer. Chem. Soc.*, **27**, pp. 474–475 (1905).

But even if it should be desired to obtain the metallic silver in a condition which may be regarded as absolutely pure for all analytical purposes, it can readily be obtained by electrolyzing a solution of silver nitrate, as shown by the work of Gooch and Perkins;[19] while if it also be desired to use precautions taken by Richards in his atomic weight determinations, we need only fuse the silver in a boat of pure lime placed in an atmosphere of hydrogen. In other words, if we adopt pure metallic silver as the standard for our volumetric solutions, we enable chemists and pharmacists to obtain such standard, even commercially,[20] in a condition not requiring further purification, or to prepare same in the laboratory with comparatively very little work. It would probably also avoid such dissimilarity of results as that seen in the case of potassium bitartrate, for example, which, as already mentioned, Parsons states that although following Bornträger's directions, he had to recrystallize three times in addition in order to prepare the pure salt; or the different results obtained by Lunge when studying Kühling's potassium tetroxalate, to which reference has already been made.

And we can also readily see why there should be such a striking difference between metallic silver as the standard and most of the other substances which have been proposed for this same purpose. For in the case of metallic silver we are dealing with an element—a substance which is undecomposable by any means at present known—whereas in the case of most of the other substances proposed as standards, we are dealing with compounds, many of which are more or less easily hydrated, some of which are hygroscopic, and nearly all of which are more or less soluble in water and hence readily affected by moisture.

The advantages of metallic silver as the ultimate standard in volumetric analysis are, however, not entirely due to its elementary nature but largely to its own peculiar properties. Thus, when com-

[19] *Zeit. anorg. Chem.*, **63**, pp. 322–323 (1909).

[20] It is interesting to note in this connection the various descriptions given to Merck's "Tested Reagents." Thus we note: Potassium tetroxalate, for use in "preparation of volumetric solutions." Sodium carbonate, anhydrous—for use as "starting material for preparation of volumetric solutions." Oxalic acid—for use in "preparation of volumetric solutions." Potassium bitartrate—for use as "starting material for preparation of volumetric solutions." Silver sheets, for use in "*standardizing* volumetric solutions." (Prices and Uses of Tested Reagents, Merck & Co., New York, 1909).

pared with such an element as iron for example (which is quite often used in standardizing $KMnO_4$ solutions), silver offers the additional advantages of being much more readily prepared in perfectly pure state, in being suitable for a volumetric process in which atmospheric oxidation can have no influence, and in being suitable for long keeping unaltered. To illustrate the last mentioned property of silver we need only recall that when at the request of Dumas, Stas [21] repeated (1890) his work on silver, he found that the silver which he used in his atomic weight determinations (probably about 1860) contained an altogether insignificant amount of gases, in no case greater than the unavoidable experimental error. In other words, although many years had elapsed between the two investigations, yet Stas apparently felt confident, and his results prove, that his silver had remained unaltered. In fact, it is quite within the limits of probability that with only ordinary precautions, metallic silver may be kept unaltered not only for decades but even for centuries. Finally, pure metallic silver as the ultimate standard in volumetric analysis would offer the additional advantages that when used in the form of bright sheets, its undiminished brightness could always be taken as a good indication, at least, of its having retained its original purity; while by using comparatively large pieces of it,[22] any possible loss of the standard substance in transferring from the container in which it is weighed to the vessel in which the analysis is carried out, would be entirely avoided.

Urged by such reasoning as the above, the writer has used pure metallic silver as the standard in volumetric analysis for some time past with very satisfactory results. The plan in general is as follows: About 0.5 Gm. of the silver, accurately weighed, is placed in an Erlenmeyer flask of about 200 c.c. capacity, about 10 c.c. of moderately strong (about 32 per cent.) nitric acid are added, and a small funnel is placed in the mouth of the flask to insure against loss of liquid by spirting. Gentle heat is applied, and when the silver has dissolved, the solution is diluted with about 25 c.c. of pure distilled water and the nitrous acid expelled by heating the solution to boiling.

[21] *Jour. Chem. Soc.*, **58**, 561 (1890).

[22] If metallic silver were generally adopted as the ultimate standard in volumetric analysis, it would be feasible to place the silver on the market as coin-like disks of uniform, accurate, and convenient weight, suitable for direct use in standardization; thus saving considerable time in the execution of the latter and further eliminating personal error.

The funnel is then washed and the washings added to the main solution. This solution is then titrated with a thiocyanate solution of about $\frac{N}{10}$ strength, using ferric alum as indicator, thus determining the exact value of the thiocyanate solution. By means of this thiocyanate solution, a tenth-normal silver nitrate solution is prepared; and the latter is then used in preparing $\frac{N}{10}$ HCl. By means of this HCl, $\frac{N}{10}$ alkali is prepared; and by means of the latter, an oxalic acid solution is standardized. The latter is then used in standardizing the permanganate solution; and by means of the permanganate solution, $\frac{N}{10}$ sodium thiosulphate is prepared, the process being essentially the same as that given in the U.S.P., only substituting the permanganate in place of the dichromate; the reason for choosing the $KMnO_4$ for this purpose, instead of the dichromate, being that a sharper end reaction may be obtained and, as pointed out by Bruhns,[23] the former has also the advantage in that the reaction is practically instantaneous. This, therefore, would give us all the necessary solutions on which is based the entire system of volumetric analysis as usually carried out.

In this connection it is also interesting to note that Rothmund and Burgstaller[24] have recently shown that in shaking the AgCl suspension with ether, in determining chlorides by means of the Volhard thiocyanate method, filtration of the AgCl is rendered unnecessary, and accurate results are obtained by direct titration of the unfiltered mixture even when the amounts of chlorine are small. And as further showing the advantages of metallic silver as the standard in volumetric analysis, we may mention the recent work of Gooch and Perkins,[25] who showed that free iodine in solution may be accurately determined through its reaction with metallic silver. Likewise, Hopfgartner[26] has shown that potassium permanganate may be standardized directly by means of metallic silver by dissolving the latter in ferric ammonium sulphate which has been acidified with sulphuric acid and titrating the ferrous salt thus formed with the permanganate solution. Finally, when we recall the present commendable tendency to refer all important work to exact standards, as may be illustrated by the work of the Hygienic Laboratory in furnishing the standard for the preparation of the

[23] *Jour. Chem. Soc.*, **90**, ii, 577 (1906).
[24] *Zeit. anorg. Chem.*, **63**, 330–6 (1909).
[25] *Ibid.*, 318–324.
[26] *Jour. Chem. Soc.*, **88**, ii, 484 (1905).

antidiphtheric serum of the U.S.P., it would seem that by adopting pure metallic silver as the ultimate standard in volumetric analysis we would pave the way for finally having such standard supplied from one source, thus making the uniformity absolutely complete. It would seem advisable, therefore, that in the next revision of the U. S. Pharmacopœia pure metallic silver be adopted as the ultimate standard for the required volumetric solutions.

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A NOTE ON THE SUBSTITUTION OF ANHYDROUS SODIUM SULPHITE FOR THE HYDRATED VARIETY GIVEN IN THE U. S. PHARMACOPŒIA.

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According to the present U. S. Pharmacopœia sodium sulphite ($Na_2SO_3.7H_2O$) should contain not less than 94 per cent. of this salt. The experience in this laboratory, however, has been that when this salt is obtained commercially it frequently contains sulphate as an impurity which is about as large in amount as the remaining sulphite. An idea as to the amount of sulphate which may be present in such samples of sulphite may be obtained from the results of an analysis[1] carried out in this laboratory on a sample of this salt which was obtained from one of the most careful and reliable firms in the country. This analysis resulted as follows:

	Found (Per cent.)
Sodium sulphite	22.05
Sodium sulphate	25.00
Water (loss on drying in vacuo at 100° C.)	52.50
	99.55

That this sample of sodium sulphite probably was up to the required standard when first prepared, but had been thus reduced in its sulphite content as the result of the lapse of time between its preparation and analysis, is indicated by the fact that a sample of this salt ($Na_2SO_3.7H_2O$) which was prepared in this laboratory and

[1] Kastle and Elvove: *Jour. Infectious Diseases*, 6, 619–629 (1909).

which on analysis immediately after preparation showed a percentage purity of 99.69, was found to have lost approximately one-fifth of its total available sulphite after standing for six months in a glass-stoppered bottle, under ordinary conditions, the bottle having been opened only a few times during this interval in order to remove small amounts of the salt. It appears also that others have met with similar experience in the examination of this salt. Thus

TABLE I

Showing the Degree of Purity of Samples of Anhydrous Sodium Sulphite Obtained from Various Sources.

Number of sample	Amount taken for analysis (gramme)	$\frac{N}{10}$ Iodine required (c.c.)	Percentage purity
1 (Commercial)	0.1260	18.25	91.25
2 "	0.1260	18.75	93.75
3 "	0.1260	19.20	96.00
4 "	0.1260	19.30	96.50
5 "	0.1260	19.30	96.50
6 "	0.1260	19.45	97.25
7 (Prepared as described by Kastle and Elvove)	0.1260	19.80	99.00
8 (Prepared and analyzed by Hartley and Barrett, using an indirect method of analysis)	0.1260		99.87

Smith, Kline and French Co.[2] report on the examination of 12 samples of sodium sulphite ($Na_2SO_3.7H_2O$) several of which contained only 90 per cent. of this salt. Likewise, Patch[3] has found all of the four samples which he examined to contain an excess of sulphate; his results showing that 100 parts of the dried sodium sulphite represented from 137 to 167 of the crystallized salt, whereas, if the latter had been of U.S.P. purity, 100 parts of the dried sulphite should have contained enough Na_2SO_3 to represent about 188 parts of the crystallized salt.

[2] Lab. Rep., S. K. and F., 1906, p. 20; from Bull. No. 58, Hyg. Lab., U. S. Pub. Health and Mar. Hosp. Ser., Wash., p. 481.

[3] Proc. A. Ph. A., **54**, 346 (1906).

On the other hand, anhydrous sodium sulphite was found, by Hartley and Barrett,[4] to be stable so long as it is kept dry, while Kastle and Elvove [5] also found the anhydrous salt to show practically no change even when kept under ordinary conditions in glass-stoppered bottles for about a month. The latter authors have also pointed out [6] the advantage that is gained by the use of anhydrous sodium sulphite in place of the hydrated salt in the preparation of Endo's [7] medium, and in this connection have also described a modification of Hartley and Barrett's method for the preparation of anhydrous sodium sulphite which increases the yield and makes it of greater general convenience to carry out. Likewise, the marked difference in the stability of anhydrous sodium sulphite, as compared with the hydrated salt ($Na_2SO_3.7H_2O$), may be seen from the results obtained in the examination of commercial samples of these salts. Thus, a sample of the anhydrous sodium sulphite, obtained from the same firm that supplied the hydrated sodium sulphite which, according to the analysis above mentioned, contained only 22.05 per cent. of Na_2SO_3, was found to be 96.5 per cent. pure Na_2SO_3. In fact, even the poorest of the samples of anhydrous sodium sulphite examined was found to contain over 91 per cent. of available Na_2SO_3, as may be seen from the results given in Table I.

That the anhydrous sodium sulphite remains practically unaltered, even when kept for a comparatively long time, under ordinary conditions, in glass-stoppered bottles, may be seen from the results given in Table II.

These results show, therefore, that even after having stood for over seven months, under ordinary conditions, in glass-stoppered bottles, none of the samples of anhydrous sodium sulphite examined, altered in its available sulphite to an extent which might be considered practically significant when compared with what takes place, under similar conditions, in the case of the hydrated salt. It would seem advisable, therefore, that in the next revision of the U.S.P., anhydrous sodium sulphite be substituted for the hydrated variety given in the present U.S.P.; and as the results given in Table I show that several firms now supply anhydrous sodium

[4] *Jour. Chem. Soc., Trans.*, **95**, 1178–85 (1909).
[5] *Loc. cit.*
[6] *Loc. cit.*
[7] *Centralbl. f. Bakt., Orig.*, 1903–4, **35**, p. 109.

sulphite in a condition of purity representing over 96 per cent. of the theory, it would seem that a minimum purity requirement of about 95 per cent. of the theory would certainly not be unreasonable.

In this connection it may also be noted that while the primary reason for the desirability of substituting the anhydrous sodium sulphite for the hydrated variety given in the U.S.P. is the great difference in their stability under ordinary conditions, there is also

TABLE II

Stability of Anhydrous Sodium Sulphite.

(Kept under ordinary conditions, in glass-stoppered bottles.)

Number of sample	Length of time kept (days)	Amount taken for analysis (gramme)	$\frac{N}{10}$ Iodine required (c.c.)	Percentage purity
1	1	0.1260	18.25	91.25
1	221	0.1260	18.00	90.00
2	1	0.1260	18.75	93.75
2	221	0.1260	18.60	93.00
3	1	0.1260	19.20	96.00
3	221	0.1260	18.85	94.25
4	1	0.1260	19.30	96.50
4	221	0.1260	18.95	94.75
5	1	0.1260	19.30	96.50
5	221	0.1260	19.05	95.25
6	1	0.1260	19.45	97.25
6	221	0.1260	19.30	96.50
7	1	0.1260	19.80	99.00
7	221	0.1260	19.60	98.00

an economic reason favorable to such change. For, inasmuch as the activity or value of the sodium sulphite depends entirely on the amount of available SO_2 which it contains, and as we can readily see that the latter would constitute a proportionately larger amount in the anhydrous salt than in the hydrated, the proposed change would, therefore, result in considerable saving in the cost of transportation. Thus a pound of the sodium sulphite of the U.S.P. ($Na_2SO_3.7H_2O$), even when absolutely pure, has only about half

the amount of available SO_2 which is available in an equal weight of the anhydrous salt, Na_2SO_3; or perhaps we may better illustrate this point by taking the actual case of the firm referred to above, from whom samples of each of these salts were obtained. The transportation charges for equal weights of these salts would ordinarily be equal; although the amount of available sulphite, Na_2SO_3, in the hydrated salt was only 22.05 per cent. of its weight whereas in the anhydrous salt it was 96.5 per cent. of its weight, thus making the cost of transporting the sulphite of the former over four times its corresponding cost in the latter case. Besides, the cost of the anhydrous salt was less than twice the cost of an equal weight of the hydrated salt, although on the basis of the available SO_2 the former is worth double the price of the latter, even if both were of an equal degree of purity; thus actually making the anhydrous salt a cheaper source for SO_2 than the corresponding hydrated salt, even if we do not consider the difference in the cost of transportation; while if the manufacture of the anhydrous salt were based on the principle on which rests the method of Hartley and Barrett,[8] namely, that crystallization of the anhydrous sulphite is obtainable by boiling its aqueous solution, the cost of the anhydrous salt could probably become reduced to even less than the present cost of the sodium sulphite of the U.S.P. Finally, the anhydrous sodium sulphite has also the advantage over the corresponding hydrated salt in that it is more suitable for the exact weighing of prescribed amounts, such as are required in the making of certain preparations, or for yielding previously calculated amounts of SO_2.

Inasmuch, however, as the disadvantage of instability applies also to the acid sodium sulphite or bisulphite, $NaHSO_3$, which is included in the present U.S.P.; and perhaps with even greater force, on account of its apparently higher degree of instability, as was indicated by an experiment tried in this laboratory, and as is also indicated by the fact that the U.S.P. purity requirement for this salt is only 90 per cent. against 94 per cent. in the case of the corresponding normal salt, $Na_2SO_3.7H_2O$; it appears desirable, therefore, to avoid, if possible, the inclusion of the acid salt in the U.S.P. as a substance having a fixed standard of purity. In fact, there appears no sufficient reason why the acid sodium sulphite might not be omitted entirely from the list of official substances, since the

[8] *Loc. cit.*

normal salt probably could replace it in most cases; and where it could not replace it directly it might replace it indirectly by using it in conjunction with an equivalent amount of a suitable acid, as hydrochloric, sulphuric, or sulphurous acid. Of course when we compare the concentration of the available SO_2 (25.4 per cent.) in the sulphite ($Na_2SO_3.7H_2O$) with that in the bisulphite (61.5 per cent.), the difference in favor of the latter is quite large, thus rendering it of especial value in all cases where a high concentration of available SO_2 is required; but when we remember that by substituting the anhydrous sodium sulphite for the hydrated sulphite of the U.S.P. we also double the concentration of available SO_2, the difference in favor of the bisulphite becomes practically negligible. Thus the bisulphite of the U.S.P. (90 per cent. purity) would have a concentration of available SO_2 equivalent to about 55 per cent., whereas the anhydrous sodium sulphite (over 96 per cent. purity in many commercial samples) would have a concentration of available SO_2 equivalent to about 49 per cent.; the difference in the concentration of available SO_2 in the latter case, therefore, could hardly affect the reaction in any given case where the bisulphite might be used as a reagent.

On the other hand, it seemed that, having the anhydrous sodium sulphite as a ready source of supply of SO_2, we might also be able to readily prepare and isolate the bisulphite whenever wanted by taking advantage of the comparatively sparing solubility of the latter in strong alcohol. In order to test this plan the following experiment was tried:

Since 1 Gm. of water will absorb[9] 0.168 Gm. of SO_2 (at 8° C. and a barometric pressure of 760 mm.), to saturate 40 Gm. of water would require 6.72 Gm. SO_2. To obtain this quantity of SO_2 from Na_2SO_3, 13.2 Gm. of the latter will be required. Since, however, the actual amount of Na_2SO_3 in the sample of sulphite used was only about 95 per cent., it would, therefore, theoretically require 13.9 Gm. of the sulphite. This, therefore, gives us an idea as to the approximate amount of sulphite required under the conditions of this experiment; hence 15 Gm. of the sulphite were used. This was placed in a distilling flask of about 250 c.c. capacity, the mouth of which was fitted with a doubly perforated stopper; one of these perforations being used for connecting with the separatory funnel,

[9] Watts' Dictionary of Chemistry, vol. 4, p. 614 (1902).

into which 30 c.c. of strong (93 per cent.) sulphuric acid were placed; while the other perforation in the stopper was used for uniting, by means of suitable tubing, the inner atmosphere of the flask with that of the separatory funnel; the arrangement, therefore, being the same as that previously used [10] for the preparation of chlorinated soda solution. The delivery tube of the flask was connected with a small Drechsel gas washing bottle, in which were placed 40 Gm. of recently distilled water. The Drechsel bottle was placed in a glass jar containing ice-water and unmelted ice, and its outlet tube was connected with a piece of glass tubing which led into a test-tube containing a little of a strong solution of sodium carbonate. After all the connections had been made, the stop-cock of the separatory funnel was turned so as to let the sulphuric acid fall slowly in drops on the solid Na_2SO_3 in the flask. Heat was not applied at the beginning of the operation, but when the current of SO_2 was observed to have weakened, gentle heating was applied to the flask, and the operation continued until practically the entire available SO_2 had been evolved. When thus carried out not even the slightest odor of SO_2 could be noticed in the room in which this operation was performed. The Drechsel and contents were weighed before and after the passage of the SO_2 into it and the increase in weight was found to be 6.8 Gm., corresponding, therefore, to 8.7 Gm. of sulphurous acid, H_2SO_3. To combine this amount of H_2SO_3 with Na_2SO_3 so as to yield the acid salt, $NaHSO_3$, it would require 13.4 Gm. of pure Na_2SO_3, or 13.96 Gm. of a sample containing 96 per cent. Na_2SO_3. The latter quantity was, therefore, added to the sulphurous acid solution in the Drechsel, the removable upper part of the latter was replaced by a cork, and the contents well shaken. It was then transferred to a beaker of about 250 c.c. capacity and 200 c.c. of alcohol added to it. The beaker and contents were then placed in the ice-water bath, the contents well mixed, and the whole allowed to remain in this bath for about 15 minutes. The precipitate formed was filtered off on a Hirsch funnel with the aid of the vacuum pump until no more liquid could be observed to drain from the funnel; the final drying being effected by pressing between layers of filter paper. The weight of the bisulphite thus obtained in the solid state was found to be over 11 grammes, representing,

[10] Amer. Jour. Pharm., **82**, 161–166 (1910).

therefore, about 50 per cent. of the theory. The filtrate, however, continued to yield further crops of the salt which, if it had been desired to collect, would have increased the obtained yield still further. An analysis of this salt showed it to be 96.5 per cent. pure sodium bisulphite, $NaHSO_3$.

It is thus seen that when having the anhydrous sodium sulphite we can readily obtain a sulphurous acid solution containing about 14.5 per cent. SO_2 (the U.S.P. requires not less than 6 per cent. SO_2); and that by adding to such a sulphurous acid solution an equivalent of the solid anhydrous sodium sulphite, we can readily obtain a very strong solution of the acid salt (which could be used as such in at least many cases where the bisulphite is required); while by adding a sufficient amount of alcohol to such an aqueous solution of the bisulphite we can readily obtain the latter even in the solid state and in a condition of higher purity than that required by the U.S.P. It would seem, therefore, that in addition to the substitution of the anhydrous sodium sulphite in place of the hydrated sulphite ($Na_2SO_3.7H_2O$) given in the present U.S.P., and the omitting of the acid salt or bisulphite from the list of substances having a fixed standard of purity, it might also be well to substitute anhydrous sodium sulphite as the source of the SO_2 in the preparation of sulphurous acid instead of obtaining the latter by the indirect, and certainly not very simple, method of reducing sulphuric acid by means of charcoal, which is the method adopted in the present U.S.P.

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NOTES ON QUININE SALTS AND OTHER CHEMICALS OF THE U. S. PHARMACOPŒIA.

BY GEORGE L. SCHAEFER.

The following notes on the solubilities of a few important quinine salts in ether and other solvents are given, for the reason that there are a considerable number of discrepancies in the literature regarding these data. I have also included a few corrections of the melting points and other tests of a few other chemicals in the U. S. Pharmacopœia, which may be of interest to pharmaceutical chemists at the present time.

QUININE HYDROBROMIDE.

Lines 21 and 22 of the U. S. P. description of this salt read: "Ammonia water added to an aqueous solution of the salt produces a white precipitate, which is soluble in a large excess of the reagent." This test cannot be carried out, except with very small traces of the salt, and ought to be omitted.

In view of this I would suggest the following modification of this test and its adoption for all the quinine salts: "Ammonia water added to an aqueous solution of the salt produces a white precipitate, which is easily soluble in ether." This would differentiate the quinine salts at once from the salts of other cinchona alkaloids.

The solubility in ether of this salt is, according to the U. S. P. 1 to 16, while it is practically insoluble or very difficultly soluble, requiring about 700 parts of the solvent for solution.

QUININE HYDROCHLORIDE.

According to the U. S. P., sulphuric acid should not produce a color with this salt. However, if the salt is treated with concentrated sulphuric acid the resulting solution is yellowish, hydrochloric acid gas being developed.

When slowly heated it melts at about 120° C. with its full amount of water of crystallization. The commercial salt containing 1–2 per cent. less water melts at about 125° C. The completely anhydrous salt melts at about 155–160° C. The latter quickly absorbs water from the air, again lowering the melting point.

There is no distinct melting point for the commercial salt, according to the larger or smaller percentage of water of crystallization in the salt, the melting point differing from 5–10° C.

The salt is not soluble in ether in the proportion of 1 to 240, but it is almost insoluble or very difficultly soluble in ether, requiring about 1000 parts of the solvent.

QUININE SALICYLATE.

Solubility in water at 25° C.....1 : 2100
Solubility in water at 80° C.....1 : 280
Solubility in alcohol at 25° C.....1 : 23
Solubility in alcohol at 60° C.....1 : 5
Solubility in ether, about.....1 : 780
Solubility in chloroform.....1 : 10

CODEINE ALKALOID.

The solubility of this alkaloid in ether is not 1 to 12½, but 1 to 25.

CODEINE PHOSPHATE.

All the preparations on the market contain only ½ molecule of water of crystallization. The salt with 2 molecules of water exists, but it is a practical impossibility to produce it for commercial purposes.

The salt with ½ molecule of water ought to be made official, being the pure commercial chemical.

DIACETYL MORPHINE HYDROCHLORIDE.

In all the publications pertaining to this salt the formula is written $C_{17}H_{17}(C_2H_3O)_2NO_3HCl$, this having reference to the anhydrous salt, which, however, cannot be made commercially. The salt, when freshly prepared from an alcoholic solution in the regular way and dried in the air, contains 3 molecules of water of crystallization. When dried at a moderate heat it becomes anhydrous, but if this anhydrous crystalline powder is taken from the drying room it absorbs quickly 1 molecule of water of crystallization from the air. Therefore, no anhydrous salt can be found on the market. The following formula ought to be adopted for this chemical: $C_{17}H_{17}(C_2H_3O)_2NO_3HCl + H_2O$, which accordingly contains 95.75 per cent. of anhydrous salt and 4.25 per cent. of water of crystallization, and which is the pure commercial salt.

STRYCHNINE ALKALOID.

Solubility in alcohol at 25° C.....1 : 150
Solubility in chloroform at 25° C.....1 : 7

STRYCHNINE NITRATE.

Solubility in water at 25° C.....1 : 55
Solubility in alcohol .....1 : 220

STRYCHNINE SULPHATE.

Strychnine sulphate does not melt at 200° C. If heated to about 250° C. it begins to get brown, and at a higher temperature it

melts with decomposition. It thus follows that no distinct melting point can be given for this salt.

Solubility in water at 25° C.	1 : 45
Solubility in water at 80° C.	1 : 9
Solubility in alcohol at 25° C.	1 : 105

SALICYLIC ACID.

This acid requires 475 parts of water at 25° C. for solution.

ACETPHENETIDIN.

The test adopted by the U. S. Pharmacopœia for the determination of the presence of acetanilide cannot be used in its present form, as even the purest acetphenetidin will not give a clear solution. If, however, the method is modified in the following way, very small quantities of acetanilide can be detected:

A quantity of 0.1 Gm. of acetphenetidin is mixed in a test-tube with 2 c.c. of a solution of potassium hydroxide, 1 to 2, and the test-tube put in boiling water for two minutes, shaking it during this time. The contents of the tube are now diluted with 4 c.c. of cold water, the mixture cooled and filtered through a small pellet of glass wool. To the resulting clear liquid 5 c.c. of solution of chlorinated soda are added. If the acetphenetidin is pure a clear yellowish solution is produced; if acetanilide is present the liquid will assume at once a slight to a dark purplish-brown color, according to the quantity of acetanilide present, the color changing gradually to yellow when allowed to stand for some time.

This test will show the presence of even less than 2 per cent. of acetanilide.

A list of official chemicals is appended for which the sulphuric acid test has been adopted. It is very important to have this test carried out in distinct proportions of the substance and concentrated sulphuric acid to get uniform results in the hands of different chemists. From practical experience I have found the proportions given in this list to be perfectly satisfactory.

PROPOSED PROPORTION OF SUBSTANCE AND CONCENTRATED SULPHURIC ACID.

Atropine	0.02 : 5	c.c.
Benzoic acid	1 : 10	c.c.
Caffeine	0.1 : 10	c.c.
Cinchonidine sulphate	0.1 : 10	c.c.
Cinchonine sulphate	0.1 : 10	c.c.
Cocaine hydrochloride	0.1 : 10	c.c.
Codeine alkaloid	0.1 : 10	c.c.
Codeine phosphate	0.1 : 10	c.c.
Codeine sulphate	0.1 : 10	c.c.
Hyoscine hydrobromide	0.01 : 5	c.c.
Hyoscyamine sulphate	0.01 : 5	c.c.
Hyoscyamine	0.01 : 5	c.c.
Morphine	0.1 : 10	c.c.
Physostigmine sulphate	0.01 : 5	c.c.
Physostigmine salicylate	0.01 : 5	c.c.
Pilocarpine hydrochloride	0.01 : 5	c.c.
Pilocarpine nitrate	0.01 : 5	c.c.
Piperine	0.1 : 10	c.c.
Quinine	0.1 : 10	c.c.
Quinine bisulphate	0.1 : 10	c.c.
Quinine hydrobromide	0.1 : 10	c.c.
Quinine hydrochloride (slightly yellow)	0.1 : 10	c.c.
Quinine sulphate	0.1 : 10	c.c.
Sparteine sulphate	0.01 : 5	c.c.
Strychnine	0.1 : 10	c.c.
Strychnine sulphate	0.1 : 10	c.c.

LABORATORY NEW YORK QUININE AND CHEMICAL WORKS.

THE ASSAY OF OINTMENT OF AMMONIATED MERCURY.

By John R. Rippetoe.

Determining the ammoniated mercury by extracting the fats by means of a volatile solvent and collecting the insoluble residue of this salt on balanced filters, or a Gooch crucible, proved to be very tedious and besides it was impossible to obtain a result that was even approximate. Ether, petroleum ether, and chloroform were the solvents used. Several filter papers of fine texture were used, but none of them seemed to be of such a character as to prevent some of the ammoniated mercury from being carried through. Extraction of the fats by means of a Soxhlet apparatus, using an extraction tube, was even less satisfactory.

Hence the following method was worked out which so far has given very satisfactory results. Weigh accurately 2.5 to 3.0 grammes of the sample into a four-ounce, wide-mouthed Erlenmeyer flask. Add 50 c.c. ether and dissolve the fats by agitation, then add 10 c.c. hydrochloric acid (10 per cent.) and 10 c.c. distilled water, and dissolve the ammoniated mercury by agitation. Transfer the solutions to a separator and draw off the acid solution. Wash the flask and separator with water until the washings give no test with silver nitrate solution for chlorides. Pass hydrogen sulphide into the combined acid solution and washings until saturated, and set aside for 15 minutes in a warm place. Collect the mercuric sulphide on balanced filters or a Gooch crucible, wash thoroughly with water, and dry to a constant weight at 100° C. The weight of mercuric sulphide obtained multiplied by 1.0837 equals the weight of ammoniated mercury in the sample taken. Working with a known amount of ammoniated mercury incorporated with the same proportion of white petrolatum and hydrous wool fat, as in the official ointment, 99.1 per cent. of the salt taken was determined, assuming the salt to have been 100 per cent. pure.

The above method should be equally applicable for the assay of the ointments of mercuric nitrate, and yellow and red mercuric oxide.

It would seem desirable that the next revision of the U. S. Pharmacopœia should have some such method of assay for the above ointments, since the present one gives a method of assay for mercurial ointment.

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ECHINACEA AND A SPURIOUS ROOT THAT APPEARED IN THE FALL OF 1909.

By John Moser, Jr., P.D.
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During the fall of 1909, a root of uncertain botanical origin was offered as echinacea to the New York drug merchants. The commercial source was St. Louis, and for a time nearly all of the echinacea offered was found on examination to be spurious. The spurious root may have been offered before this time, but if so it has not to our knowledge been reported.

A search of the literature on the subject, which is not abundant, failed to bring out any information that would indicate that the root in question had been previously recognized as spurious, or that would throw any light whatever on its probable botanical source. (See note.)

The spurious root when in the entire state differs in certain features from echinacea, but yields a powder that has a very similar appearance, and in this form its detection is extremely improbable without a microscopic examination.

Considerable difference of opinion as to the medicinal value of echinacea exists, as certain recent reports indicate. That the drug is attracting much attention is shown by the fact that the demand is constantly increasing, while the market supply of the true root is now practically exhausted.

Echinacea contains 1 per cent. or more of an acrid resinous substance, and is said also to contain an alkaloid. When tasted it exhibits certain characteristics which would lead one to believe it is far from inert. However this may be, it is certain that the spurious root cannot be expected to represent in any way the activity of the true drug.

A comparative study of echinacea and the spurious root has been made in our laboratory, with a view of bringing out data which will aid in the detection of the spurious when in powdered form or when present as an admixture with powdered echinacea. The principal difference was found in the sclerenchymatous tissue as will be later pointed out.

Two closely related plants of the *Compositæ* contribute to the

supply of echinacea root: *Brauneria purpurea,* the purple cone flower, and *Brauneria pallida,* pale purple cone flower, the former growing from Western Pennsylvania and Virginia to Illinois and southward, and the latter from Illinois and Wisconsin southward. They are perennial herbs with stout and nearly simple stems, terminated by a single large head. The name cone flower is derived from the conical torus, which is covered with a lanceolate, spiny-tipped chaff, longer than the disk florets. The ray florets are about 5 cm. long, drooping, pistillate but sterile, and usually rose-purple in color.

The dried root is the part used medicinally, and has the following characteristics: Root of vertical growth, usually in pieces 5 to 20 cm. long, 0.5 to 3 cm. in diameter; crown branched, the branches somewhat annulate above and with stem scars, rarely stem remnants present; dark brown to blackish externally, slightly tapering, sometimes twisted, deeply longitudinally wrinkled; fracture short, weak; bark thin, 0.5 mm. or less in diameter, and brownish; wood radiate from the numerous greenish-yellow wood wedges; parenchymatous tissue dark gray to blackish; odor distinctly and peculiarly aromatic, characteristic; taste pungent, somewhat acrid, producing a profuse flow of saliva, followed by a tingling sensation and slight numbness.

The powder may be described as follows: Light grayish-brown; tracheæ numerous, lignified, 15 to 20μ in diameter, with simple pores, or 20 to 50μ in diameter and scarlariform; wood fibres usually single or in groups of 2 or 3, 250 to 600μ long, 20 to 30μ in diameter, the average being 300μ long and 25μ in diameter, strongly lignified and with numerous simple pores; cork cells irregular and deep reddish-brown; parenchyma of cortex irregular and with yellowish- or reddish-brown resinous contents; fragments of resin cells with suberized walls and a pale yellowish resin which is changed to greenish-yellow by KOH, breaking up into small globules and apparently dissolving. When mounted in concentrated H_2SO_4 the fragments of parenchymatous tissue assume a reddish-brown color which gradually deepens. Stone cells are absent.

The spurious root has the following characteristics: Somewhat conical crown, 3 to 10 cm. long, 1 to 4 cm. in diameter, tapering upward and terminated by a stem scar or stem remnant; dull brown to blackish externally and finely wrinkled; base spherical and giving rise to several fusiform roots of horizontal growth, 5 to 15

cm. long, 0.5 to 2 cm. in diameter, dark brown to blackish externally and longitudinally wrinkled; occasionally with fibrous rootlets, sometimes also fusiform, and 5 to 10 cm. long; fracture short-fibrous, rather tough; bark 0.5 to 1 mm. thick, brownish and with numerous groups of stone cells; wood grayish, radiate with yellow wood wedges; odor faintly but distinctly aromatic; taste momentarily pungent, slightly bitter and acrid.

The powder is light gray in color and also exhibits the following characteristics: Tracheæ numerous, lignified, 15 to 50μ in diameter, with simple or bordered pores, occasionally with scarlariform markings; wood fibres 200 to 300μ long, 12 to 30μ in diameter, strongly lignified and with simple pores; stone cells numerous, usually in groups, isodiametric and 25 to 40μ in diameter, or elongated, 50 to 150μ long, 25 to 40μ in diameter, very thick walled and with numerous simple pores; cork cells reddish-brown; parenchyma of cortex regular and with a brownish or reddish resinous content; fragments of resin cells with pale yellowish resin, less numerous than in echinacea. KOH and concentrated H_2SO_4 have an action similar to that on echinacea.

In the examination of powdered echinacea containing some of the spurious root, the isolation of the sclerenchymatous fibres by means of Schultze's macerating solution or by digestion with 10 per cent. KOH solution, was found to facilitate the work greatly and to render it possible to detect minute quantities of the spurious root.

NOTE.—Since the completion of this article the attention of the author was called to the editorial "Is Echinacea Valueless" in *The Druggists' Circular,* February, 1910, p. 70. It is stated that a St. Louis friend of the editor called attention to the fact that a large quantity of the root of *Parthenium integrifolium* had been collected in that vicinity and disposed of in the St. Louis market. He also expressed the fear that it was intended as a substitute for or adulterant of echinacea. From the brief description which is given of parthenium it would appear that its characteristics are very similar to, if not identical with, the spurious root herein described. However this cannot be definitely stated until an opportunity is afforded to examine an entire plant at the flowering period.

It is believed that the facts here presented will enable the manufacturer to insist upon being supplied with the true echinacea, the identity of the spurious root being of secondary importance.

RAPID CHEMICAL FILTRATION COMPARED TO SLOW SAND FILTRATION.

By William G. Toplis.

On three previous occasions [1] it has been my privilege to address this body on the subject of water purification—each time some phase of slow sand filtration was considered.

To-day the subject is again water purification, but this time we consider a different side, which is known as rapid filtration. In order that we may have a better understanding of the difference between the two methods, it seems proper to restate, briefly, the basic principles of slow sand filtration. This method is favored for the purification of municipal water supplies and the objects sought to be accomplished are: first, the removal of suspended matter, and, second, the decomposition of organic matter in solution. The first is simple, the mud being strained out as the water percolates through the sand. The second is much more complex, and is brought about through the growth of living vegetable organisms, known as bacteria, that thrive within the sand bed, and are attached to the grains of sand, in such quantity that they actually form a coating over the surface of each grain of sand. The sand bed is about four feet deep. The water is controlled in its passage through the sand and is allowed to proceed at a rate of from three to six million gallons per acre per twenty-four hours. This means that each square foot of area filters about ten cubic feet of water in twenty-four hours at the three million rate. Now as the strained water passes through the fine spaces between the grains of sand in the filter it carries the dissolved organic matter together with some atmospheric oxygen, also in solution, to the bacteria growing within the sand bed. Here the organic matter is absorbed by these growths, and it furnishes pabulum for their existence and propagation. The extreme limit of organic contamination in drinking water is perhaps represented in urea, and as the greater includes the less, the treatment of urea will cover all kinds of organic contamination. Urea is composed of four elements: carbon, hydrogen, oxygen, and nitrogen. As the contaminated water passes slowly through the sand the

[1] Amer. Jour. Pharm., **74**, 67, Feb., 1902; **76**, March, 1904; **81**, 220, May, 1909.

bacteria absorb the dissolved matter and digest it and resolve it into the simple oxides of the elements composing it, viz., carbon becomes carbon dioxide (CO_2), hydrogen and oxygen combine to form water (H_2O), nitrogen is finally changed into compounds of nitric acid.

Chemical analyses of water properly treated by the method thus described prove the statements to be facts, and the water wholly acceptable from both hygienic and æsthetic considerations. There is no better method known for the purification of municipal water supplies when properly conducted. It will be noted, however, that the conditions are rigid and inflexible, and that the method is suitable for but one purpose and limited to that one, especially so because of the large areas of land necessary for its execution.

The purification of municipal water supplies is but one of the many water purification problems, which problems seem to be of unending variety, and call for wide knowledge and experience for their successful handling. The variety of requirements for industrial purposes calls for a system of great flexibility, one that can be quickly adapted to changing needs, and deliver large volumes of treated water in little time and by apparatus that must be confined to restricted space. These conditions are quite the reverse of those necessary in slow sand filtration.

There are two types of rapid filtering apparatus, one of the open variety known as the "gravity filter," and one which is closed and constructed in a metallic case, known as a "pressure filter." The closed type is used where filtered water is to be delivered to a level higher than that of the filter, and the open type is used where the water may flow from the filter by gravity to a point of delivery below the level of the filter.

The same principles are involved in the operation of both types; and both types are built on the same general plan though the pressure filter must be provided with a cover bolted upon it. The most common form is that of a cylinder, of any suitable material. It may be of wood, metal, or concrete, provided with proper inlets and outlets. At the bottom, inside of the container, a special line of piping is arranged. Upon the upper surface of this piping a number of sand valves are placed. The sand valve is the most important feature connected with this system of filtration. Its function is to retain the sand in the filter but allow the water to pass freely out after filtration, and in addition to this allow the freest ingress of water

at the bottom of the filter for washing purposes; and, further, the sand valve must be so constructed that it will automatically open and discharge any particles of sand that may effect lodgement in its parts.

The action of these filters is wholly chemical. In the reaction between alum and bicarbonate of calcium is found the agency to which this method owes its efficiency. All river and spring waters have hardness to a greater or less degree, and very few, if any, are devoid of it. Hardness is commonly due to the presence of lime compounds dissolved in the water, generally in the form of bicarbonate of calcium. If a solution of alum be added to such water, being careful to keep the lime compounds in excess, an interchange between the alum and lime follows, with the result that aluminum hydrate is precipitated, carbon dioxide is evolved, and sulphate of calcium produced, the latter remaining in solution. The objective point of this reaction is the production of aluminum hydrate. This substance when freshly precipitated forms a very voluminous, gelatinous, white precipitate that embraces all suspended matter in a sticky envelope and holds it in a layer upon the sand. The water passes through at a rate greatly in excess of the slow sand method, about 100 to 1. So thoroughly is the filtering performed that the water is quite as brilliant as the most carefully prepared distilled water.

The result in this respect is very often better than the slow sand filter attains. This is not surprising when it is remembered that the particles of clay suspended in water are often less in size than bacteria, and frequently are as small as one one hundred thousandth of an inch in diameter, as has been determined by the Massachusetts State Board of Health.

After the filter has been operating for a period it becomes noticeably clogged, resulting in what is technically known as loss in head—to remedy this condition the filter is washed by passing in at the bottom filtered water through the sand valves, at such a rate that the sand is turned over and lumps and adhesions are broken up, and all of the adhering mud and separated matter are washed out of the filter into the sewer. This is accomplished in from five to ten minutes and the filter again performs its duty when the flow of water is directed downward through the sand.

As stated before no oxidizing action takes place in this method of filtration, but recently successful effort has been made to bring

this about in a chemical way as follows: Calcium hypochlorite in solution was introduced into the water before filtration in the proportion of two or three parts per million. The reaction that follows is precisely the same as that employed in urinalysis in the estimation of urea in which nitrogen is evolved as gas. The result of this as compared with the oxidation change in the slow sand filter is, instead of forming nitric acid and increasing nitrates, the nitrogen, as gas, is thrown off and hydrochloric acid is produced, increasing chlorides. Other changes are the same. In addition to this the hypochlorite has the effect of increasing the bacterial efficiency to an extraordinary degree.

Another interesting adaptation of this method of filtration may be cited in conditions such as are met in the Passaic River, New Jersey, at Passaic. The water of the river at this city is black, colored by the refuse discharged into it from the silk dye works at Paterson. In addition to the dye, all of the sewage of the City of Paterson empties into this stream, forming a malodorous combination. The problem was to deodorize and decolorize the water and to free it from bacteria to a large degree. The first was accomplished by aeration and sedimentation. The second by taking advantage of the property of aluminum hydrate to form lakes with dye colors, that, becoming insoluble in water, are easily filtered out and these, together with the bacteria, were readily removed by the filter, working at a rate of 1000 cubic feet of filtered water per square foot per twenty-four hours. The water resulting from this treatment was suitable for use in bleaching white goods and the manufacture of white paper.

Another problem quite different was met in the treatment of the water supply at Fort Hancock, Sandy Hook, New Jersey. This water was so strongly impregnated with iron that it was altogether unfit for drinking. Tea was turned into ink, and for laundry purposes it was impossible. The Government engineers had endeavored to free it by oxidation and sedimentation, but it was found that all of four days were required for oxidation and not less than two weeks were necessary for complete sedimentation, conditions that were altogether impracticable. Finally, the chemical filter was installed. The water was treated with small quantities of calcium hydroxide in solution and then filtered at the rate of 400 million gallons per acre per twenty-four hours, which is equal to 10 cubic feet in twelve minutes per square foot of surface as compared with

10 cubic feet in twenty-four hours which is the slow sand filtering rate for each square foot of surface. The result was a water entirely palatable and faultless for laundry work.

Each of the preceding examples described applications of principles with the effluent as the objective. The following case is one where the filtered water is run to waste in the sewer and the contamination saved, just reversing the conditions.

At Mt. Vernon, New York, there is a large silver manufacturing establishment. For various reasons considerable silver finds its way into the wash water used by the silversmiths. This waste is allowed to run into a sedimentation basin where it is treated with sodium chloride, and allowed to subside. The water after standing is pumped into a filter where any suspended matter is caught, and after this process has been carried far enough the filter is washed and the washings returned to the sedimentation basin, and the clear water is again directed into the sewer. The saving to the manufacturers is $5000 per annum, the cost of which is $150 for one year's operating expenses.

One other and very important adaptation of rapid filtration is that in connection with so-called water softening. This process consists in removing from the water dissolved salts of calcium or magnesium that may be present. The handling of this matter requires precise manipulation as will be understood from the character of the reactions involved—because excess of the reagents would also produce hardness; hardness it will be remembered is commonly due to the presence of bicarbonate and sulphate of calcium. The first step is to add a slight excess of calcium hydroxide to the water. The result of this is to neutralize the half bound carbonic acid of the bicarbonate of calcium and precipitate it as neutral calcium carbonate. After an interval sodium carbonate solution is added, when any excess of calcium hydroxide is changed to neutral carbonate of calcium and the sulphate of calcium is precipitated also as carbonate—the resulting sodium sulphate remains in solution. After this treatment the water is conducted to a filter where the precipitates are removed and the water is passed on practically free of hardness. This treatment is capable of reducing water of extreme hardness at a very rapid rate, to about 2 degrees of hardness. This is the limit because neutral calcium carbonate is soluble in water to this slight extent; refinement in apparatus is absolutely essential but it is quite practicable in competent hands.

CONSERVATION AND THE CHEMICAL ENGINEER.*

By Samuel P. Sadtler.

We have heard much in the last year or two concerning the conservation of our natural resources and we shall, I feel certain, hear much more in the next few years, as the facts elicited from the preliminary studies of the subject come to be understood by the public at large. The importance of the subject will grow correspondingly as the matter is studied by the thoughtful citizen, and his appreciation of it will in time be reflected in the activity of the statesmen at Washington in the proposing of remedial measures.

Conservation let us note, however, represents the third stage in the history of the development of natural resources.

The first stage is exploration or discovery. This is the era of the prospector and has given us in this country some famous episodes. We need only recall the discovery of gold in California in 1849 and the way in which it operated to attract adventurous spirits from the older parts of our country, or the repetition of the same story with the discovery of the rich gold deposits on the Yukon and at Nome in Alaska.

The first discovery of rich petroleum deposits of Western Pennsylvania in the early sixties brought, similarly, multitudes of prospectors or "wildcatters," as they came to be known locally, and this experience has been repeated also from time to time as great petroleum gushers or powerful gas wells have been reported in various sections of the country, resulting in the opening of new fields, as in Ohio, Indiana, Kansas, Texas, and Oklahoma.

The second stage is exploitation, when these lavish gifts of nature are worked with a view mainly of increasing production and usually in a wasteful way with no thought of the exhaustion of the supply.

As illustrations of this stage we need only cite the way in which our coal mines have been worked. In Bulletin 394 of the U. S. Geological Survey (papers on the conservation of mineral resources) we find the statement that "it has been estimated that the actual

* Presidential address delivered at the second annual meeting of the American Institute of Chemical Engineers in Philadelphia, Dec. 8, 1909; and reprinted from *Metallurgical and Chemical Engineering*, **8**, p. 9, Jan., 1910.

loss or waste sustained through coal left in the mines in conducting mining operations amounts to 50 per cent. of the quantity produced and marketed." Worse than this, when the Anthracite Coal Waste Commission made its report in 1893 they estimated that "for every ton produced one and a half tons were lost."

One of our most valuable gifts of nature is the natural gas, which is associated more or less directly with petroleum. It is a fuel of the greatest value, being nearly pure hydrocarbon in its composition. Yet we find in the same Bulletin of the Geological Survey before referred to the following: "As to the amount of natural gas which is being wasted daily, no accurate statistics have been attempted and the judgment of Dr. I. C. White, State Geologist of West Virginia, may well be accepted to the effect that no less than 1,000,000,000 cubic feet of gas are wasted every twenty-four hours. Of this, undoubtedly the larger part is wasted in the production of oil." This waste, Dr. Day of the Geological Survey says, "practically equals the annual consumption of natural gas reported for 1907. This waste should furnish light for half the urban population of the United States."

The exploitation of our once great timber resources and the resulting denudation of great tracts of land and the evils to the soil which have followed in the train of this ruthless waste have been so graphically portrayed by the U. S. Forestry Bureau and others recently that I need not more than allude to this case of reckless extravagance.

It is not my intention, however, to take up this evening the question of the conservation of our natural resources and the absolute need thereof, as so ably developed in recent reports of the "National Conservation Commission," the Forestry Bureau, and other official publications, nor yet the part played by the chemist in this conservation of natural resources which has been so ably reviewed by Dr. Bogert in his recent Presidential address before the American Chemical Society.

What I would like to do is to indicate that these same three stages of exploration or discovery, exploitation or effort at production, and finally conservation, are to be seen in the history of every great chemical industry, and to point out, that, while it is the part of the chemical engineer to aid in the exploitation step, what is still more important is his part in counselling and indicating how the wholesome influence of conservation can be applied so as to broaden

and extend the scope of the industry, to maintain and add to its remunerative character, and to give it stability and promise of permanence.

Let us illustrate this view by examples, and take first the great petroleum industry to which reference has already been made in speaking of the era of exploration when the petroleum fields were first outlined by the work of the prospector and driller. The second stage of exploitation began to draw upon the help of those who were chemical engineers, in fact if not by title. The development of the distilling and refining processes came first. Starting with the old cheese-box still with its circle of heating grates under it, there was a change, following upon the discovery of the "cracking process" as applied to crude oil, to the present form of cylindrical still with its movable cover to regulate the chilling of the vapors during the latter part of the operation. This simple feature in distilling enables the refiners to get 75 per cent. or more of burning oil from the crude petroleum instead of the 45 per cent. of a normal fractional distillation, while producing a residuum which can be advantageously distilled for paraffin oils.

The proper control of the acid and alkali treatment of the crude distillates, the change from the old forms of presses for paraffin scale to the modern filter press, the introduction of bone-black filtration for reduced oils and residuums all contributed to develop and expand enormously the several parts of the industry to which they were applied. With these improvements in large scale methods went the inauguration of improved testing and analytical methods, so that uniformity of product so essential for sound business development was secured.

Let us turn now to the newer evidence of the work of the chemical engineer in the way of conservation as illustrated in this same industry. The collection and utilization for fuel purposes of the uncondensed gas from the distillation of crude oil is one of the important economies that has been generally adopted. The working up of the sludge-acid and recovery of not only sulphuric acid but of valuable side-products is now a feature of the larger refineries. The introduction of clay filtration to improve the quality of the heavier grades of oils is an important advance as well as a step of economy. The production of gas oils from the less valuable crude oils has also become an important industry, as these are of great value for gas-making and gas-enriching. The more thorough utilization

of residues is also a feature of recent years. From these residues are now made excellent road oils for the aid of the good roads movement. The petroleum pitch is all utilized also, partly for electric light carbons and partly for fuel purposes. Most promising of all, however, is the result, not as yet fully attained, but most certain of solution in the immediate future, viz., the utilization of crude petroleum of the lesser valuable kinds and residuums in internal combustion engines for the development of power.

A second typical industry is that of coal distillation. We have already spoken of the wastage in the mining of coal. It is not necessary here to speak of the corresponding waste in its utilization as fuel. We will speak solely of the distillation of coal. This treatment may be carried out from either one of two points of view, and the exploitation in each case has been pushed with great energy, utilizing all available chemical and engineering skill. The first is the distillation for the manufacture of illuminating gas. While the mechanical side of this process has advanced steadily, particularly after the introduction of regenerative firing and mechanical stoking, the chemical side did not advance so rapidly. While the coal-tar is no longer thrown away, unless it be in very isolated localities, the proper chemical utilization of this tar has lagged behind both in this country and in England. On the other hand, the true conservation of this valuable side-product and the development of its possibilities has advanced in a notable degree in Germany, the home of the coal-tar industry. Here the research chemist and the chemical engineer have gone hand in hand in the building up of a great industry or rather two industries based upon the utilization of the coal-tar, the manufacture of the coal-tar dye colors, and the manufacture of synthetic medical preparations possessing valuable therapeutic characteristics. Besides these most important and highly developed illustrations of conservation, we have, however, some minor utilizations of coal-tar or products from the same that deserve mention. Thus the manufacture of creosote oils for the preservative treatment of wood, the roofing-pitch and tar-paper manufacture and the use of pitch in the biquetting of coal are illustrations of value given to the coal-tar and its products.

The thorough extraction of the ammonia and the impurities like the cyanides from the ammoniacal liquor and the production of commercially valuable products from them is, moreover, an accomplishment in the way of conservation. The utilization, too, of the

gas carbon for the manufacture of electrode carbons, battery plates and for electric light carbons is another illustration of this work.

The second method of distilling coal is that for the production of coke for metallurgical purposes. This has been developed or more properly exploited to such a degree that, according to the "Mineral Resources of the United States," published by the U. S. Geological Survey, the production of coke for the year 1907 was 40,779,564 tons, of which, however, 35,171,665 tons were produced in beehive ovens. In these as is well known, only the fixed carbon of the bituminous coal is saved and all volatile constituents including gas, tar, and ammonia are absolutely wasted. On the other hand, 5,607,899 tons of coke were produced in by-product recovery ovens and the value of the by-products (gas, tar, and ammonia) obtained therefrom amounted to $7,548,071. It is easy to reckon from this what the loss was on the 35,171,665 tons of coke made in beehive ovens. In fact, the article on "Coal," in Bulletin 394 before referred to says with reference to this, "at the prices which prevailed in 1907, the value of the by-products wasted in beehive coke-ovens was a little over $55,000,000."

But the result achieved by the chemical engineer in the working of this by-product over represents more than merely saving certain by-products. The gas produced can be separated by the perfect control of the method into "poor gas" for fuel purposes and "rich gas" for illuminating purposes, so that the highest economy or conservation of values is thereby attained.

Another industry in which the chemical engineer has worked first for the purpose of exploitation and later for conservation of material and values is the starch industry. Starch, as we all know, is one of the most widely distributed vegetable products and has always played a great part in the world's supply of food. In Europe, it is potato and wheat starch, in the United States it is corn starch, and in tropical countries it is rice, tapioca, sago, etc., that are the important varieties of this cereal food. Not only has the production of starch been developed, however, for food purposes, but enormous quantities of the starchy substances serve as the starting point in the fermentation industries. Then we have the use of both starch and its alteration product, dextrine, in the textile industries and the production of glucose as the product of the hydrolysis of starch, and the manufacture of nitro-starch and its utilization in the explosives industry. All of these industries have attained a high

degree of perfection by the application to them of a chemical understanding of the nature of starch and its alteration products and the devising of processes by which the several reaction changes could be carried out with exactness and economy. What that means as applied to one single branch of the starch industry, those of us who had the opportunity on the occasion of our meeting last June to go through the works of the Corn Products Company at Edgewater, N. J., can appreciate. The glucose production of the United States in 1907 is stated to have been 800,000 tons, requiring 40,000,000 bushels of corn as raw material. But besides the production of the solid grape-sugar and the liquid glucose for a great variety of uses, the separation of the germ of the corn from the starchy portion has made possible the production on a large scale of corn-oil, a product adapted for a wide range of uses—from soap making to the manufacture of rubber substitute.

Turning now to inorganic chemistry for an illustration, we have a splendid example of the work of the chemical engineer in the direction of conservation in the case of the natural and artificial nitrate industry, to which latter the Germans have already given the expressive name of "air-salpetre." The great source of nitrate for forty or more years past has been the deposits on the west coast of South America, furnishing the so-called Chili salpetre or sodium nitrate. This has been drawn upon increasingly until in 1908 the quantity shipped was 1,730,000 tons, valued at $87,500,000. But the Chilean deposits are far from being inexhaustible. It is estimated that if the annual consumption increases merely by 50,000 tons, and this is to be reasonably expected, from thirty to forty years will see the practical exhaustion of this supply. So in 1899, Sir Wm. Crookes startled the industrial world by calling attention, in what the newspaper men would call a "scare-article," to the nitrogen problem and the necessity of maintaining a supply of nitrogenous plant food if the world's food requirements were to be met. Crookes pointed out the way of relief when he said "the fixation of atmospheric nitrogen is one of the greatest discoveries awaiting the ingenuity of chemists. It is certainly deeply important in its practical bearings on the future welfare and happiness of the civilized races of mankind." The chemical engineer has responded nobly to this demand for conservation of available nitrogenous material by the working out of practical methods for the manufacture of what we called "air-salpetre." It must not be supposed, however, that success was easily obtained.

Not only were the usual experimental difficulties to be overcome but, as Prof. Bernthsen has well shown in his address before the London International Congress of Applied Chemistry in May last, there are theoretical difficulties of the most serious kind standing in the road of ready fixation of atmospheric nitrogen and oxygen in the form of nitrogen oxides convertible into nitrates. So it happened that the first large enterprise of this kind, the process of the Atmospheric Products Company, established at Niagara Falls, had to be given up as commercially unavailable. This was followed by the Birkeland and Eyde process, started in Norway with the cheapest water power to be found, and this is still in successful operation. A few years later (in 1905) the Schönherr process was worked out by the Badische Anilin and Soda Fabrik, also using Norwegian water power and still later the Pauling process at Gelsenkirchen, near Innsbruck, in Tyrol. The Schönherr process seems to be the most successful.

It produces a 40 per cent. nitric acid, calcium nitrate, or calcium or sodium nitrite, according as the absorption part of the process is modified. All of the processes mentioned require the cheapest electrical energy, which can only be developed by cheap water power, and thus far best developed in Norway. Prof. Bernthsen states, however, that probably within a few years the annual output of calcium nitrate or " air-salpetre " will reach 100,000 tons. As this involves first the fixation of atmospheric nitrogen, and second the use of " white coal," as water power is sometimes fancifully called, it is a true lesson in conservation of natural resources, especially as it also enables us to replace a rapidly disappearing natural product.

Closely related to this recently developed inorganic industry of air-salpetre is the slightly older one of calcium carbide and its offshoot the cyanamide or " nitrolime " industry. With the production of calcium carbide in the electric furnace in 1892 by Willson and the publication of Moissan's work on the electric furnace in 1894, sprang into existence a great industry, as the acetylene gas lighting made possible thereby had great advantages. Isolated lighting plants, acetylene lamps for automobiles and carriages, luminous buoys and signals, a new material for lampblack manufacture, and other utilizations all were rapidly developed. The perfecting of the furnaces and the process for this manufacture of carbide enlisted the attention of electrical and chemical engineers and at the present time the world's production of calcium carbide is estimated to be about

200,000 metric tons per annum, largely in countries like Norway, Italy, and Switzerland where cheap water power is available, as well as in the United States at Niagara Falls and Sault St. Marie. This production, however, for the time being outran the demand for carbide for acetylene lighting.

Relief from over-production by finding new outlets and utilizations is always to be preferred to closing of works already in operation, so chemical engineers have found new possibilities for calcium carbide. By far the most important of these is the production from calcium carbide of calcium cyanamide by the action of nitrogen gas, as worked out by Drs. Frank and Caro. We have here an exothermic reaction in which nitrogen is absorbed by the carbide with the production of calcium cyanamide and carbon. This takes place at a temperature of from 800° to 1000° C., much below that needed for the carbide manufacture. Not only can all the nitrogen of this cyanamide be converted into ammonia by decomposition with steam, but it is gradually decomposed by the chemical and bacteriological constituents of the soil into ammonia, which becomes fixed by the vegetable mould and is so held. The cyanamide is also convertible into calcium cyanide by melting with fluxes, into dicyandiamide for dye-color manufacture, into urea, guanidine, and other hitherto relatively expensive organic compounds. The dicyandiamide is already used as a "deterrent" in smokeless powder manufacture, reducing the temperature of the explosion without diminishing explosive force, and the crude calcium cyanamide with certain fluxes under the name of "ferrodur" is employed for case-hardening of iron and steel.

The statement is made that the works for the manufacture of "nitrolime" now in operation or in course of construction have a capacity of 166,000 tons per year.

The illustrations of conservation, whether from the point of view of better utilization of materials, or the production of new and varied products, or the recovery of what were waste products, could be greatly extended did time allow.

We might refer to the way in which sulphur recovery has been worked out in the alkali industry, or to the manganese recovery in connection with the chlorine production from manganese dioxide, so that "recovered manganese" is to-day a most valuable article of commerce. Or we might note the saving resulting from the manufacture of reclaimed rubber, but these and similar illustrations

of the conservation theme as influenced by the work of the chemical engineer will have to be passed by for the present.

That there are numerous problems as yet unsolved of equal and possibly greater importance than some of these discussed will also be conceded by those possessing even a moderate acquaintance with chemical industries.

One of these problems, for instance, is the recovery of the valuable constituents of the waste liquor of the sulphite wood-pulp process. A German authority states that every litre of this waste liquor contains 120 Gms. of organic material as against 10 to 15 Gms. of mineral substance. Dr. A. Frank estimated that in 1904 there was wasted in this way in Germany 300 million kilogrammes of organic material, concerning which we know that it has value in several directions. In this country, the sulphite wood-pulp process has also an extensive development and the same waste liquor is run off into our streams.

A somewhat different problem, but one of even greater importance, is the loss of valuable metals in smelter smoke and fumes. The American production of bismuth is not over 10,000 lbs. a year and considerable amounts of bismuth and bismuth compounds are imported every year. Yet it is estimated in the forthcoming report of the U. S. Geological Survey for 1908 that 880 lbs. of bismuth per day are being thrown off in the smoke of the great Washoe smelter at Anaconda, Mont., and with this also go copper, lead, zinc, arsenic, and other mineral products. One way of saving much of this lost material is pointed out in noting that the replacing of smelting methods by electrolytic methods, possible in some cases, allows these metals to be recovered from the deposited slimes.

In conclusion, let us emphasize the fact that our chemical industries need not merely development or exploitation, but if they are to continue to flourish as we are drawn more and more into international competition they must have the newest and best results of chemical research applied by the experienced chemical engineer. New and better materials must be sought, better processes evolved, economies effected at all possible stages, and waste products carefully looked after. The most successful chemical industries in the world, which show the highest scientific and technical development and which are steadily expanding and throwing out branches, are those of the great German chemical companies. Organizations like the Badische Anilin and Soda Fabrik, which have by their employ-

ment of both research chemists and chemical engineers effected industrial revolutions, one after the other, like the introduction of artificial indigo, the contact sulphuric-acid manufacture, and last of all the production of air-salpetre or artificial nitric acid and nitrates, are those which reap the rich commercial rewards and for the reason that they have done the work and earned them. The hope of a successful American chemical industry lies in the same direction.

ABSTRACTS OF THESES ON CHEMICAL SUBJECTS.*

By J. W. Ehman.

Phenyl Salicylate (R. J. Wotring).—Chiefly a study of the liquefaction of mixtures of salol with other substances. Salol and menthol may be mixed in the proportion of one molecular weight of the former to three of the latter, also in the proportion of three to two molecules to form a dry powder; two molecules salol to three menthol produce a damp powder and equal molecules of each liquefy.

Salol and camphor in different proportions produce either pasty mixtures or liquids.

Salol with either phenacetine, antipyrin, or salicylic acid will result in dry powders, but the addition of a small amount of camphor to either mixture will cause liquefaction. Salicylic acid with camphor alone forms a dry powder.

Three molecules of salol to one of thymol or one of salol to three of thymol form pasty mixtures; in other proportions they liquefy.

Either one or three molecules of salol to two of chloral hydrate form moist powders, but in other proportions dry mixtures result.

Salol and resorcinol in different proportions form dry powder. With acetanilid a dry mixture results, but the addition of antipyrin causes liquefaction.

Either beta-naphthol, pyrogallol, or sodium salicylate mixed with salol results in dry mixtures. While salol with either antipyrin or resorcinol forms dry powder, when all three are mixed a pasty mass results.

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* The experimental work embodied in these theses was performed in the chemical laboratory of the Philadelphia College of Pharmacy.

Diluted Nitrohydrochloric Acid (A. A. Platt).—In view of the time required in its preparation and the poor keeping qualities of the diluted acid, it is recommended that it be prepared when required by simply diluting the strong acid. Six samples were obtained in drug stores, and assayed for free chlorine. One sample, known to have been prepared within a few days, assayed 1.542 per cent. Cl; the others from 0.257 to 0.514 per cent., average 0.334 per cent.

Experiments were made to ascertain the effects of heat in hastening the preparation of the acid. The reaction appeared to be complete in ten or fifteen minutes, and, after dilution, assayed the same percentage of free Cl as an acid made in the usual way and allowed to stand for twenty-four hours before dilution, namely, 1.5 to 2 per cent. The freshly made diluted acid deteriorated rapidly on standing in a warm place exposed to light.

Diluted nitrohydrochloric acid made by diluting some specimens of the strong acid obtained from drug stores assayed from 1.565 per cent. to 5.5 per cent. free Cl.

Some Points of Difference between Gum and Wood Turpentine (S. S. Jacobs).—Specific gravity and refractive index presented no essential difference. As to optical rotation, either gum or wood turpentine may rotate to the right or left, depending upon its source. In carrying out fractional distillation the chief point of difference appears to be that oil from the gum ceases to distil at 165° C., while the wood variety continues to distil up to 185° C., leaving in either case a very small residue. The specific gravity, optical rotation, and refractive index of the different fractions were too variable for definite conclusions to be drawn therefrom. The only distinctive difference between the fractions of the two varieties appears to be the characteristic odor peculiar to each.

Sulphurated Lime (P. M. Davis.)—Of five samples assayed, only one, taken from a sealed package obtained from a wholesale house, contained as much as 55 per cent. calcium sulphide. The author experienced great difficulty in preparing a satisfactory sample from commercial calcium sulphate, but had no difficulty when a chemically pure sulphate was used.

Stramonium (H. W. Eakle).—Leaves were collected from plants, full grown but before flowering, others from plants after flowering but before deterioration, and others were obtained in the wholesale market with time of collection not stated. Tinctures were prepared from the recently dried leaves and were then assayed.

The first specimen assayed 0.0176 per cent. mydriatic alkaloids, the second 0.02048 per cent., and the third 0.0324 per cent.

ZINC STEARATE (C. E. Hoffman).—Of four samples examined, two on ignition left a residue of 15.5 per cent., one 11.4 per cent., and the fourth 9 per cent. The stearic acid liberated from the third had a melting point of 60° C. and that from the fourth was yellow in color and melted at 72° C.

A sample prepared from zinc acetate and soap met the requirements of the U.S.P. A sample prepared by forming a soda soap with the stearic acid and treating this with zinc sulphate produced a satisfactory preparation.

TINCTURE OF IODINE (Ernest A. Noedel).—Analyses of seven samples of tincture of iodine obtained in Philadelphia and vicinity. Iodine per 100 c.c. ranged from 4.522 Gm. to 7.172 Gm., average 6.455 Gm. One specimen, that containing the lowest amount of iodine, contained no potassium iodide. The others contained from 4.08 Gm. to 5.16 Gm. KI per 100 c.c., average 4.67 Gm.

CORRESPONDENCE.

A CORRECTION.

TO THE EDITOR, AMERICAN JOURNAL OF PHARMACY:

Please note, that in the article about "Solubility of Alkaloids, etc.," published in the last issue of your paper, there is a typographical error. Instead of "quinine *hydro*phosphite" it should read "quinine *hypo*phosphite." The first named combination, of course, does not exist, and the error ought to be corrected.

Very truly yours,

GEORGE I. SCHAEFER.

April 22, 1910.

PHILADELPHIA COLLEGE OF PHARMACY.

MINUTES OF THE ANNUAL MEETING.

The annual meeting of the College was held March 28 at 4 P.M. in the Library. The President, Howard B. French, presided. The minutes of the quarterly meeting held January 4, were read and approved. The minutes of the Board of Trustees for December 7, 1909, January 4, and February 1, 1910, were read by the Registrar, and approved.

The President delivered his annual address, from which the following items of information are abstracted.

PRESIDENT'S ADDRESS.

The condition of the property in general is very good, numerous repairs having been made during the year. The internal telephone system has been repaired, the push buttons having been removed and replaced by a switchboard, so that the phones are now in first class order. The chemical lecture room which lacked proper ventilation has been remedied by placing an electric fan in the southeast corner, which has proved very successful in securing proper ventilation. The hot-house has been completed, and the Professor of Botany and his assistants have added a small addition to it.

The hot-house has been of material advantage in enabling the Professor of Botany to carry over during the winter about 150 interesting economic plants. These have been used as exhibits during the lectures, and have proven of great advantage to the students, enabling them to familiarize themselves with plants yielding official drugs. The Professor has in addition also had access to one of the largest hot-houses near the city, enabling him to exhibit plants of unusual interest to the students.

The Course in Operative Pharmacy has been unusually successful. The time given to laboratory work has been doubled in the Third Year Course, and nearly so in the First Year Course. The Special Course in Dispensing has also been materially increased.

The Course in Commercial Training has been of unusual interest, a number of lectures by men actively engaged in commercial pursuits having been given.

There is an increase of 40 students over the preceding year. In the Chemical Laboratory 85 students from the three classes have been doing individual work, and 29 third year students are doing thesis work. There have been 26 students in Special Chemistry, four of whom felt themselves sufficiently qualified to take positions of profit, and 44 other students are taking special courses.

During the year six active members have died, in the death of two of whom the College has sustained more than an ordinary loss, viz., Mahlon N. Kline and Thomas S. Wiegand.

The continued activity of the Alumni Association is much appreciated and highly commended. At the reunion of the Alumni Association held last May the Class of 1884 presented to the College a weather observatory barometer, which is to be followed shortly by an aneroid barometer. They also established a Memorial Scholarship.

In conclusion the President expresses his appreciation of the efforts of all who have actively co-operated with him, and hopes that the members, the Faculty, and others interested in the prosperity and advancement of the College, will work together in concord and harmony, having but one purpose in view, and that is, the success of the College.

The address was attentively listened to and at its close was warmly applauded.

REPORTS OF COMMITTEES.

COMMITTEE ON PHARMACEUTICAL MEETINGS.—The meetings have been held regularly during the year, various members presiding. A number of the members presented papers or addresses and participated in the discussions, and quite a number of others, not members, several of whom were from other cities, also presented papers and took part in the discussions. The minutes have been regularly published in the AMERICAN JOURNAL OF PHARMACY and reports have been furnished the leading drug journals.

Professor Kraemer, who has acted as Secretary of the Committee on Pharmaceutical Meetings for the past ten years, submitted the following letter:

According to Article XI of the By-Laws of the College, "A recorder shall be elected annually at the Pharmaceutical Meeting in May to issue the notices, prepare business, and record the proceedings of these meetings, and

to make selections therefrom for publication in the JOURNAL." While I am willing to act as recorder or secretary up until the meeting in May, I desire to be relieved of this work, and that another recorder be selected at that time. I am not clear from the By-Law whether it is necessary for the recorder to be a member of the Committee or not.

I am willing to serve on the Committee, but desire to be relieved of the details and responsibilities of the work, particularly as the meetings come at a time when I have class-work, and make this statement at this time in order that it may be properly considered.

I may say that while the meetings are not as well attended by the members of the College as they might be, they are a source of great strength to the College, and must serve to stimulate all our members who read the printed reports of them, and besides serve to attract and interest others who are not members of the College.

In conclusion, I may say that it would indeed be unfortunate if these meetings should ever be discontinued or fail to be conducted on the high plane which has characterized them from the time of their inception.

Respectfully yours,

HENRY KRAEMER.

PUBLICATION COMMITTEE.—The AMERICAN JOURNAL OF PHARMACY has been issued regularly during the year. There is an increase in the amount received from advertisers and quite an increase in the amount received from subscribers. This is a gratifying feature, showing that with the advances in pharmacy and allied lines, the JOURNAL is coming to be more appreciated, particularly by analytical workers.

EDITOR'S REPORT.—As a result of the activity of the members of the American Pharmaceutical Association, particularly in the various branches of the association, and also in the various State pharmaceutical associations, some of the best papers that have been contributed to American pharmacy have appeared in the AMERICAN JOURNAL OF PHARMACY during the past year. Some 61 papers have been published, including seventeen on analytical-chemical subjects, five on strictly pharmaceutical subjects, twenty-seven on Pharmacopœial matters and related subjects, others on pharmacognosy, pharmacology, biological subjects, besides biographical and memorial articles. In addition 33 book reviews were published, as also reports of the annual meetings of the American Pharmaceutical Association, the American Medical Association, the National Wholesale Druggists' Association, the British Pharmaceutical Conference, the Twelfth International Congress on Alcoholism, the Sixteenth International Medical Congress, and other associations.

The quarterly review of the progress in pharmacy continues to reflect the advances abroad as well as in this country.

CURATOR'S REPORT.—The Museum is in good condition and has received a number of donations during the year, the following being the donors: Howard B. French, Charles H. LaWall, M. I. Wilbert, Smith, Kline and French Co., D. H. Hage, James P. Lengel, and E. H. Gane. The historical and general collections are growing in number and importance and soon additional case-room will be required.

Acknowledgments of having received certificates of election to honorary membership were received from Surgeon-General Walter Wyman and Professor O. A. Oesterle.

The members went into executive session at 4.30 P.M. and continued in session till 5 P.M., when the following appointments were announced by the President:

DELEGATES TO THE AMERICAN PHARMACEUTICAL ASSOCIATION: Joseph P. Remington, F. E. Stewart, O. W. Osterlund, William McIntyre, and William L. Cliffe.

DELEGATES TO THE PENNSYLVANIA PHARMACEUTICAL ASSOCIATION: C. B. Lowe, William E. Lee, William McIntyre, Charles H. LaWall, H. L. Stiles, Joseph P. Remington, F. P. Stroup, Jacob M. Baer, Theodore Campbell, and Charles Leedom.

DELEGATES TO THE NEW JERSEY PHARMACEUTICAL ASSOCIATION: George M. Beringer, C. B. Lowe, Henry Kraemer, H. L. Stiles, and Theodore Campbell.

COMMITTEE ON BY-LAWS: George M. Beringer, Joseph W. England, and C. A. Weidemann.

The resignation of Theodore L. Gamble, associate member, was accepted.

A letter was received from Mrs. Isadora E. Kline acknowledging the receipt of the "In Memoriam" resolutions on the death of her husband, First Vice-president Mahlon N. Kline.

Professor S. P. Sadtler presented to the College on behalf of the family of the late Rev. Dr. Schaeffer a very ancient hydrometer —probably a century old—formerly used by Doctor William Ashmead, a physician and druggist of Germantown. A vote of thanks was tendered the donors.

The report of the Committee on Nominations was read. Messrs. Jacob M. Baer and Theodore Campbell were appointed tellers, who, after a ballot was taken, reported the election of Howard B. French,

President; R. V. Mattison, First Vice-president; Joseph L. Lemberger, Second Vice-president; Richard M. Shoemaker, Treasurer; A. W. Miller, Corresponding Secretary; C. A. Weidemann, Recording Secretary; Joseph W. England, Curator; and Henry Kraemer, Editor. Trustees for three years: Samuel P. Sadtler, William L. Cliffe, Henry Kendall Mulford. Publication Committee: Samuel P. Sadtler, Henry Kraemer, Joseph W. England, Joseph P. Remington, Martin I. Wilbert, Miss Florence Yaple, and Charles H. LaWall. Committee on Pharmaceutical Meetings: Joseph P. Remington, C. B. Lowe, Henry Kraemer, William L. Cliffe, William McIntyre.

C. A. WEIDEMANN, M.D.,
Recording Secretary.

ABSTRACTS FROM MINUTES OF THE BOARD OF TRUSTEES.

January fourth, 1910.—Fourteen members were present. The Committee on Announcement reported that another issue of the *Bulletin* would soon be published; and it was suggested that a brief outline of the activities of the College be published therein, also extracts from the special lectures being delivered in the College.

February first, 1910.—Fourteen members present. The Committee on Property was authorized to have repairs made to the intercommunicating telephone system. A communication was read from the Athletic Association and they also submitted a petition favoring athletics, which had been signed by 405 students. A general discussion followed, many of the members strongly advocating that the Board of Trustees establish a Department of Athletics in the institution. The letter and petition were referred to a committee for their consideration and report at a future meeting.

C. A. WEIDEMANN, M.D.,
Recording Secretary.

MARCH PHARMACEUTICAL MEETING.

The stated pharmaceutical meeting of the Philadelphia College of Pharmacy was held Tuesday, March 15, 1910, at 3 P.M., Mr. W. L. Cliffe presiding.

A paper by Dr. George L. Schaefer, chemist for the New York Quinine and Chemical Works, Ltd., on "Solubility of Alkaloids of Cinchona Bark and their Salts," was read, in the absence of the

author, by Freeman P. Stroup, Ph.G. (see April number of this JOURNAL, p. 175).

Prof. Joseph P. Remington said that there are several things to be considered in discussing a paper of this kind, and stated that there are a number of methods for determining solubilities, and that investigators find differences in the solubilities of chemicals due to the differences in methods. He advocated the establishment of standard methods for solubilities, melting points, and other constants. He also called attention to the various alkaloidal assay methods, and said that the Pharmacopœia is specific in this respect, as, for example, under colchicum corm, where it is stated that the percentage of alkaloid is that obtained " when assayed by the process given below." The subject of solubilities was also discussed by Frederic Rosengarten and Messrs. Beringer and Cliffe.

George M. Beringer, Ph.M., presented " A Note on Cardamom and Oil of Cardamom " (see April number of this JOURNAL, p. 167), and exhibited samples of the genuine oil which had been furnished him by different firms.

In discussing this paper, Professor Remington asked what would be the advantage in introducing the oil of cardamom into the National Formulary, and into what preparations it would enter? He said that cardamom is used on account of the flavor, and if the proposal was to replace the official cardamom fruit by the oil the preparations would not be as satisfactory to physicians. He stated that the essential oils are largely adulterated and prone to deterioration, especially under the varying conditions under which they are kept in pharmacies throughout the country, and stated that it was on account of the deterioration of oils of lemon and orange that the fresh peel had been introduced into the Pharmacopœia.

Mr. Beringer stated that it was not the intention to replace cardamom fruit for use in the tincture, but to furnish an oil for elixirs in order that physicians might have a choice of these. He said that he had been manufacturing elixirs for twenty years in which cardamom oil was used in small quantities and in such manner as to give a blended flavor. Mr. Beringer stated that the keeping quality of the oil appeared to be well established, oils which he had kept for several years under favorable conditions, in a darkened closet, showing no perceptible change.

J. J. Bridgeman, P.D., said that he had been using an oil of cardamom in prescription work which he knew to be at least four

years old, and that it is still of good quality both as regards flavor and odor.

William G. Toplis, Ph.G., presented a paper on "Rapid Sand Filtration Compared to Slow Sand Filtration" (see p. 227) and in this connection exhibited a model of a "sand valve," and demonstrated the chemical process involved in the purification of water by the use of alum. To show the practical efficiency of rapid sand filtration, Mr. Toplis also read a report on a bacteriological and chemical investigation which he had made of the operation of the filter plant recently installed at Plattsburg Barracks, N. Y., by Hungerford & Terry, Inc., of Philadelphia.

Mr. Cliffe stated that in making milk of magnesia with the filtered water of either the Delaware or Schuylkill River, which is ordinarily clear, the preparation has a yellow color, and that the use of distilled water made the process an expensive one for the retail pharmacist. He then inquired of Mr. Toplis whether in his opinion the entire process outlined by him would render the water of such a degree of purity as to fit it for use in the making of milk of magnesia, which question Mr. Toplis answered in the affirmative. Otto W. Osterlund, P.D., spoke of the same difficulty, and stated that he had found it advisable to abandon the manufacture of milk of magnesia.

Mr. Beringer stated that he makes hydrated oxide of bismuth by an inverted percolation process, which he said is in reality a process of dialysis. He remarked on the difficulty of removing the ammonia in the magma by decantation, stating that much less water is required by his process than in the official method, and that a constant layer of water can be kept above the magma until the process is completed by use of the dropping bottle. He stated, also, that he obviates the undue expense connected with the manufacture of this preparation by manufacturing his own distilled water. For the clarification of tap water he suggested the use of magnesium carbonate or light calcined magnesia as a filtering medium, and stated that sometimes the cloudy appearance of the tap water is due to a disturbance of the lining of the pipes. The speaker also pointed out that in the chemical examination of water, it is desirable for the chemist to have a knowledge of the chemical purification undergone by the water, as, otherwise, supposedly objectionable elements, such as chlorine, resulting from the purification, would be considered natural deleterious ingredients.

Others taking part in the discussion of this subject were Professor Remington and Messrs. Boring and Poley.

A paper on "Echinacea and a Spurious Root That Appeared in the Fall of 1909" by John Moser, Jr., P.D., was presented in abstract by Professor Kraemer, the author not being present (see p. 224).

Mr. Toplis called attention to a method which he has been using in the making of *syrup of ferrous iodide,* in which the bright iron wire of the official formula is replaced by reduced iron, the syrup being of a beautiful green color. He stated that the reaction is very prompt, the time required for the combination of iron and iodine in quantities to give 500 c.c. of syrup being eight minutes, the rise in temperature during the reaction being 18° C., and that the entire process may be completed within one hour. In order to overcome the generation of an excessive amount of heat in the making of larger quantities of syrup, Mr. Toplis suggested that a flask of ample proportions be used, that all of the iodine be added to the water first, and that the iron be added in small successive portions with vigorous agitation after each addition, which method, it was claimed, provides for the dissipation of the heat as rapidly as it is generated.

The chairman directed attention to books, manuscripts, pharmaceutical journals, including bound volumes of the AMERICAN JOURNAL OF PHARMACY from 1854 to 1877, and some specimens of drugs and pharmaceutical preparations, which belonged to our late fellow member, J. B. Moore. Professor Kraemer stated that Mr. Francis B. Hays, of New York, had written him stating that he had obtained through the kindness of Mr. Moore's daughter, Mrs. H. H. Watkins, and son, Rev. J. J. Joyce Moore, both of Philadelphia, letters of the late Albert E. Ebert and Prof. John M. Maisch for the Historical Section of the American Pharmaceutical Association, and also that they would be glad to make a similar disposal of the remainder of their father's pharmaceutical collection, and that, accordingly, he had procured the collection for the College. Of the books the following may be mentioned as of special interest: Richerand's Elements of Physiology, English translation, 1823; The American Dispensatory, by John Redman Coxe, M.D., 1831; Jourdan's Pharmacopœia Universalis, English translation, 1833; Notes of Lectures on the Theory and Practice of Medicine delivered at Jefferson Medical College by John Eberle, M.D., 1834; New Conversations on Chemistry by Thomas P. Jones, M.D., 1839; Dial of the Seasons by Thomas

Fisher, 1845; Treatise on the Practice of Medicine by George B. Wood, 1849.

A motion by Professor Remington, seconded by Professor Kraemer, heartily thanking Mrs. Watkins and the Rev. Mr. Moore for their generous donation, was adopted.

FLORENCE YAPLE,
Secretary *pro tem.*

PENNSYLVANIA PHARMACEUTICAL ASSOCIATION.

TO THE MEMBERS OF THE PENNSYLVANIA PHARMACEUTICAL ASSOCIATION:

On the 28th day of June next we hold our thirty-third annual meeting at Buena Vista Springs.

The Membership Committee realize the importance of a large addition to our number this year. Other State associations have been going forward rapidly, and we feel that this should be our banner year, and there is no good reason why it should not be if every member would try to secure at least one new member. The coming year will be an important one in legislative matters.

If every druggist could be informed touching what benefits he may derive by having our Legislative Committee look after our interests, he certainly would come to the conclusion that it is the best investment he makes (and to think, that only two dollars is all that he is required to pay). In addition—he has the proceedings forwarded him without additional cost—and it is self-evident that if he will read them carefully he will be very much benefited in many ways.

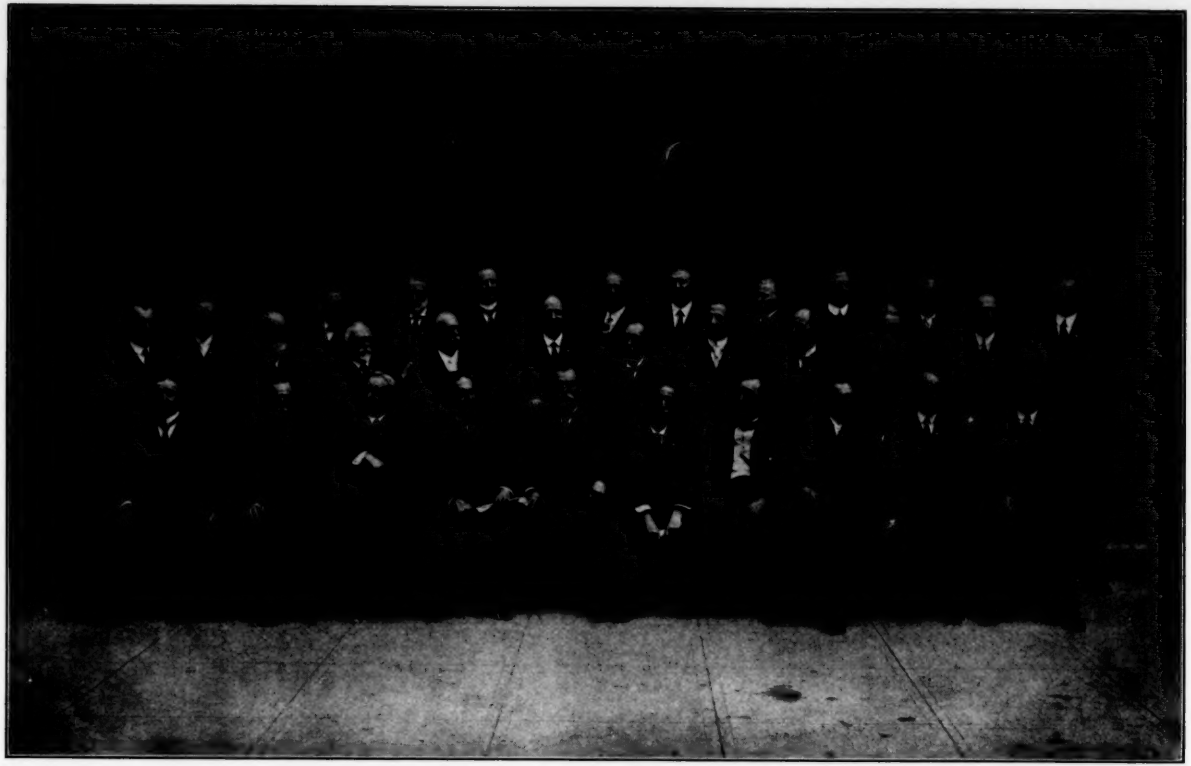
No doubt you are well posted as to the text of this letter, but this is only a reminder from the committee as to what we feel is your duty to your brother druggist.

We enclose herewith a copy of a circular letter, which the Executive Committee have sent to all non-members of the association in the State. A little missionary work on your part will materially aid in bringing those in your State within the fold. Will you do it?

Enclosed please find "blank application." If in need of more, write our Secretary, Mr. Heffner, or myself.

Yours fraternally,
WM. E. LEE.

SOME OF THE OFFICERS OF THE U. S. PHARMACOPŒIAL CONVENTION, MEMBERS OF THE BOARD OF TRUSTEES, AND MEMBERS OF THE COMMITTEE OF REVISION 1900-1910.



Diehl Sadtler Hare Sayre Gregory Stevens Kremers Hallberg A. R. L. Dohme
Scoville Good Squibb Caspari Payne Remington Lyons Coblentz Marshall Haines Kraemer
L. Dohme Lengfeld Davis Wilcox Wall C. E. Dohme Meissner Simmons Whelpley Beal